CHAPTER IV

RESULTS AND DISCUSSION

According to theory, the graft copolymerization of vinyl monomer onto any trunk polymer is always accompanied by homopolymer formation. The grafted products of the present work were thus characterized by an IR technique. This is to detect the presence of the grafted products after the removal of homopolymer.

4.1 CHARACTERISTICS OF THE GRAFTED SILK FIBRES BY INFRARED SPECTROMETRY

The results of the infrared spectra of N,N'-MBA, ungrafted silk fibres and the grafted silk fibres in the form of KBr pellets are shown in Figures 4.1a - 4.1c. The assignment is given below.

The IR-spectrum of N,N'-MBA in Figure 4.1a shows the following important peaks:

Wavenumber, cm^{-1}		Assignment
3300	:	N-H stretching
3050	:	C-H stretching

Wavenumber, cm^{-1}	Assignment
2950, 2850	: $-CH_2$ asymmetric stretching, $-CH_2$ symmetric stretching
1660, 1620	: C=O stretching
1540	: N-H bending
1410, 1380	: C-H bending
1230, 1120	: C-N stretching
990,960,900	: =C-H out-of-plane bending

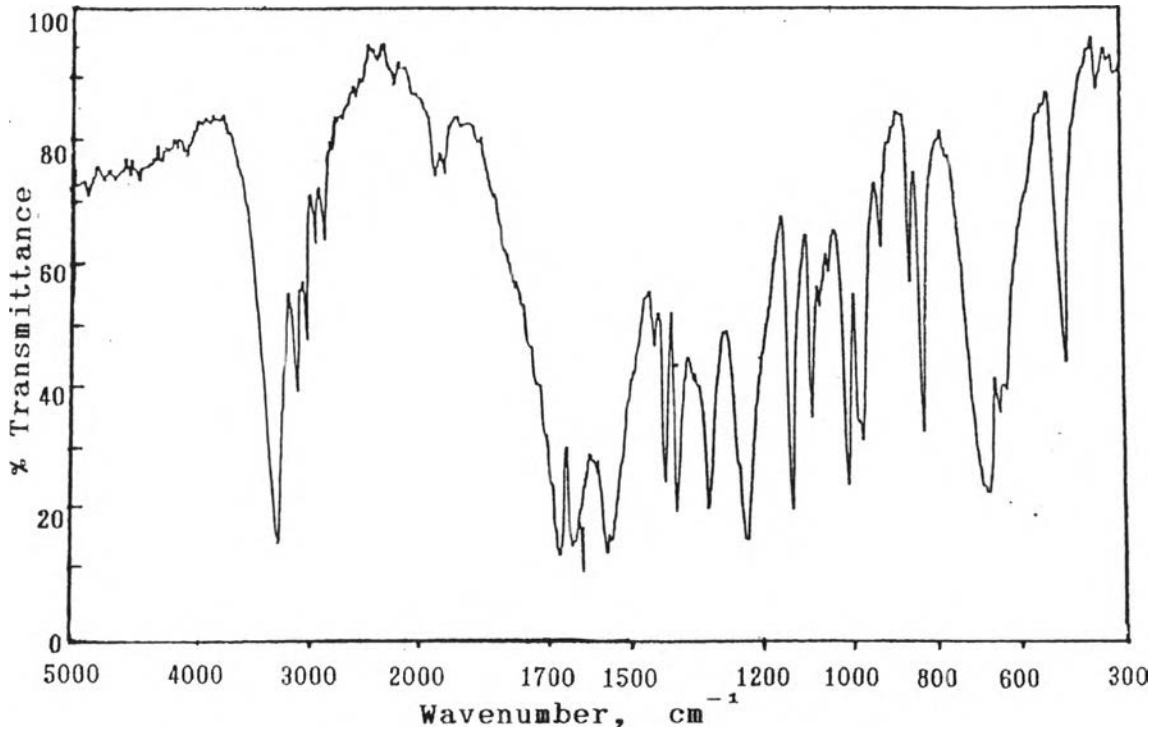


FIGURE 4.1a IR-spectrum of N,N'-MBA

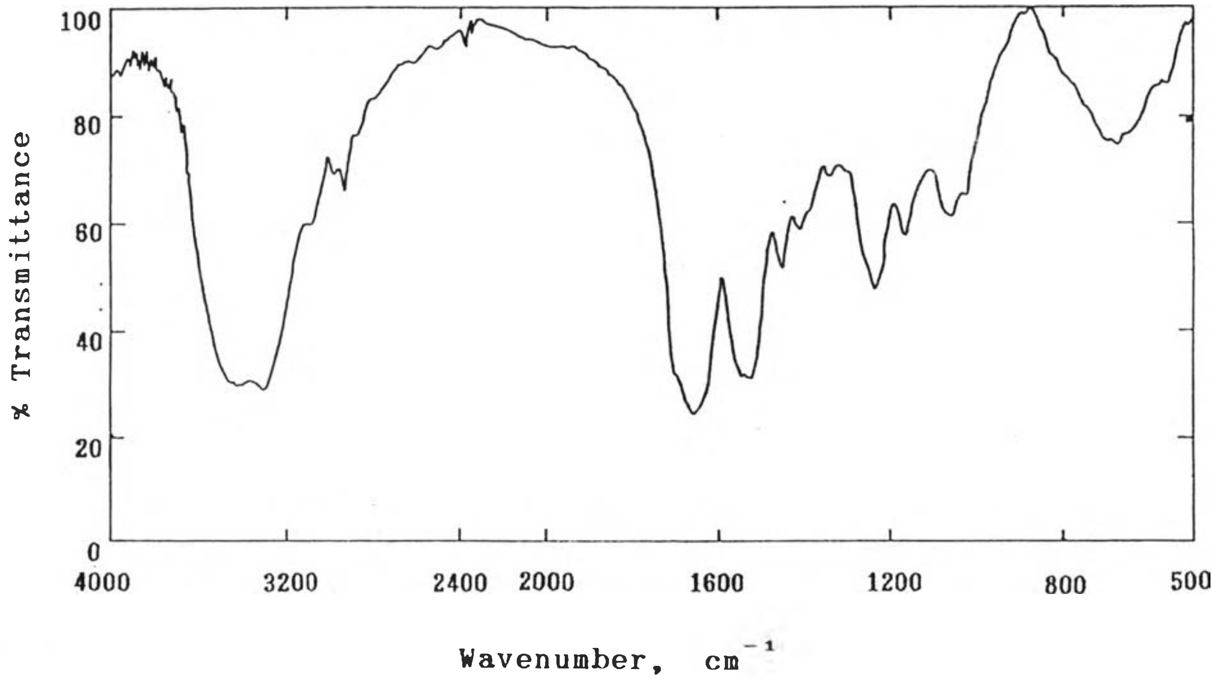


FIGURE 4.1b IR-spectrum of ungrafted silk fibres

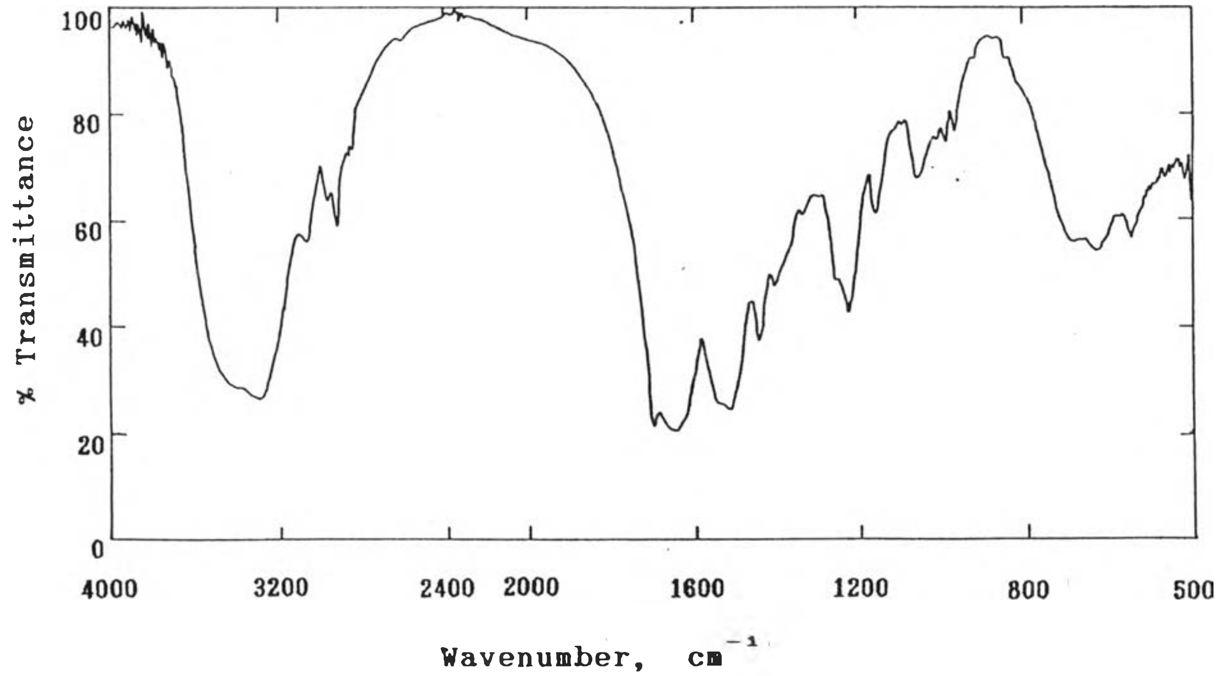


FIGURE 4.1c IR-spectrum of N,N'-MBA grafted silk fibres

The IR-spectrum of ungrafted silk fibre in Figure 4.1b shows the following important peaks:

Wavenumber, cm^{-1}		Assignment
3300	:	N-H stretching
2831	:	$-CH_2$ symmetric stretching
1655	:	C=O stretching
1527,1466,1406	:	N-H bending
1232, 1165	:	C-N stretching

The IR-spectrum of N,N'-MBA-grafted silk fibres in Figure 4.1c shows the following important peaks:

Wavenumber, cm^{-1}		Assignment
3300	:	N-H stretching
2928	:	$-CH_2$ asymmetric stretching
1657	:	C=O stretching
1516, 1448	:	N-H bending
1231, 1166	:	C-N stretching
998, 976	:	=C-H out-of-plane bending

Obviously, several distinguished peaks observed in the grafts indicate the occurrence of the graft copolymerization in which the absorption peaks of the =C-H out-of-plane bending occur at 998 cm^{-1} and 976 cm^{-1} as the evidence of the starting materials [Appendix D].

The graft copolymerization of N,N'-MBA onto the silk fibres in this research was investigated under the aqueous medium using Mn(acac)$_3$ as initiator. The rate of grafting was determined by varying the monomer concentration within the range of 2.5 x 10^{-3} to 15.0 x 10^{-3} mole-l^{-1} and by varying the initiator concentrations within the range of 0.5 x 10^{-3} to 2.5 x 10^{-3} mole-l^{-1}.

According to the research of grafting of N,N'-methylenebisacrylamide onto silk fibres using the vanadyl-acetylacetonate complex in aqueous medium by K. C. Gupta and Sharad K. Gupta [4], the grafting copolymerization in this work thus kept constant the concentrations of NaLS and HClO$_4$ at 2.0 x 10^{-3} mole-l^{-1}, and at 7.5 x 10^{-3} mole-l^{-1} respectively. The reaction time required 2hrs with the temperature at 50°C. Based on these conditions, the highest percentage grafting can be obtained.

The grafting reaction seems to be a complicated polymerization involving several vital parameters which can affect its efficiency. The following are the detailed investigations of such parameters.

4.2 EFFECT OF CONCENTRATION OF MANGANESE (III) ACETYLACETONATE ($Mn(acac)_3$) ON GRAFT YIELD

The result of percentage grafting under various concentrations of $Mn(acac)_3$ as an initiator is tabulated in Table 4.1.

The effect of the concentration of Mn $(acac)_3$ within the range of 0.5×10^{-3} to 2.5×10^{-3} mole-l^{-1} on the grafting of N,N'-MBA onto the silk fibres is shown in Figure 4.2.

Due to the complexity of the system, statistical analyses are useful to help indicate the most significant parameter.

According to Table 4.2a, the correlation coefficient (r) between the data of the percentage grafting and the concentration values of $Mn(acac)_3$ within the range of 0.5×10^{-3} to 2.5×10^{-3} mole-l^{-1} was 0.7150. It indicates that there is a possible linear-relationship between $Mn(acac)_3$ concentrations and percentage grafting in the same direction, but to characterize the influence of $Mn(acac)_3$ concentrations on the percentage grafting is questionable. Therefore, regression analysis is neccessary.

TABLE 4.1 Effect of concentration of Mn(acac)$_3$ and N,N'-MBA on grafting of N,N'-MBA onto silk fibres

Run	X1 [a] (mole-l^{-1}) x 10^{-3}	X2 [b] (mole-l^{-1}) x 10^{-3}	X3 [c] (mole-l^{-1}) x 10^{-3}	Y1 [d] (%)	Y2 [e] (%)
1A	0.5	2.5	5 X 0.5	4.0	0.0
1B	1.5	2.5	5 X 1.5	4.2	1.8
1C	2.5	2.5	5 X 2.5	7.2	0.9
2A	0.5	5.0	5 X 0.5	1.5	0.3
2B	1.5	5.0	5 X 1.5	3.5	0.0
2C	2.5	5.0	5 X 2.5	7.5	5.3
3A	0.5	7.5	5 X 0.5	5.3	9.7
3B	1.5	7.5	5 X 1.5	6.3	11.2
3C	2.5	7.5	5 X 2.5	5.8	13.7
4A	0.5	10.0	5 X 0.5	3.2	0.0
4B	1.5	10.0	5 X 1.5	2.8	1.3
4C	2.5	10.0	5 X 2.5	5.1	17.5
5A	0.5	15.0	5 X 0.5	2.7	0.0
5B	1.5	15.0	5 X 1.5	5.8	25.3
5C	2.5	15.0	5 X 2.5	5.9	25.4

[a] = Mn(acac)$_3$; [b] = N,N' -MBA; [c] = Glacial acetic acid

[d] = percentage grafting; [e] = percentage of homopolymer

([d] and [e] are 2 duplicates within 10% CV)

under the set condition of [HClO$_4$] = 7.5 X 10^{-3} mole-l^{-1}, [NaLS] = 2.0 X 10^{-3} mole-l^{-1}, temp. = 50°C and time = 2 hrs

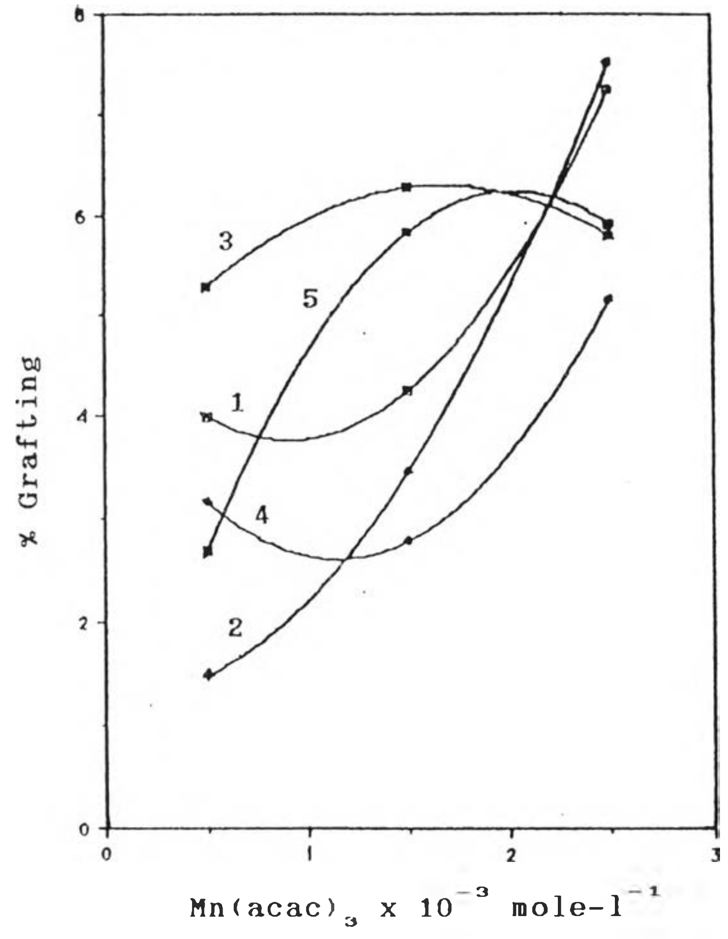


FIGURE 4.2 Effect of Mn(acac)$_3$ concentration on variation of % grafting

□ 1 R = N,N'-MBA = 2.5 x 10^{-3} mole-l^{-1}

◆ 2 R = N,N'-MBA = 5.0 x 10^{-3} mole-l^{-1}

▣ 3 R = N,N'-MBA = 7.5 x 10^{-3} mole-l^{-1}

◇ 4 R = N,N'-MBA = 10.0 x 10^{-3} mole-l^{-1}

■ 5 R = N,N'-MBA = 15.0 x 10^{-3} mole-l^{-1}

(Reaction condition : 50°C and 2 hrs)

TABLE 4.2a The correlation coefficient (r) between variables and properties

	X1	X2	Y1	Y2	Y3	Y4	Y5(S)	Y5(K)	Y6(S)	Y6(K)	Y7
X1	1.0000	0.0000	0.7150	0.4840	-0.4286	-0.5173	-0.0069	0.1948	-0.1551	0.1947	0.0000
X2	0.0000	1.0000	-0.0723	0.5983	-0.4786	-0.1511	-0.4287	0.0174	-0.4163	0.0190	-0.7599
Y1	0.7150	-0.0723	1.0000	0.5065	-0.1703	-0.3634	0.3883	0.0698	0.3932	0.0699	0.4523
Y2	0.4840	0.5983	0.5065	1.0000	-0.5557	-0.6532	0.1561	-0.0311	0.2082	-0.0303	-0.7510
Y3	-0.4286	-0.4786	-0.1703	-0.5557	1.0000	0.6286	0.0419	0.0842	0.0150	0.0836	0.8750
Y4	-0.5173	-0.0172	-0.3634	-0.6532	0.6286	1.0000	-0.3830	0.2249	-0.3860	0.2245	0.9277
Y5(S)	-0.2801	-0.2629	0.3883	0.1561	0.0419	-0.3830	1.0000	-	0.9617	-	0.2186
Y5(K)	0.1948	0.0174	0.0698	-0.0311	0.0842	0.2249	-	1.0000	-	1.0000	0.6957
Y6(S)	0.3509	-0.1499	0.3932	0.2082	0.0150	-0.3860	0.9617	-	1.0000	-	0.0960
Y6(K)	0.1947	0.0190	0.0699	-0.0303	0.0836	0.2245	-	1.0000	-	1.0000	0.6955
Y7	0.0000	-0.7559	0.4523	-0.7510	0.8750	0.9277	0.2186	0.6957	0.0960	0.6955	1.0000

1-tailed signif.: * -.01 ** -.005

where: X1 = Manganese (III) acetylacetonate

X2 = N, N'-methylenebisacrylamide

Y1 = percentage grafting

Y2 = percentage of homopolymer

Y3 = tensile strength

Y4 = percentage elongation

Y5 = quantity of dyestuff fixed on silk fibres: (S) = Supranol, (K) = Kayacyl

Y6 = percentage exhaustion: (S) = Supranol, (K) = Kayacyl

Y7 = thermal decomposition temperature

wherever this "-" shows, correlation is not taken into account

TABLE 4.2b Multiple regression between variables and properties

Dependent variables	Independent variables	Result	Conclusion
Y1	X1	sig F = 0.0027 F = 13.5996	- X1 is highly significant to Y1
Y2	X1	sig F = 0.0676 F = 3.97609	
Y3	X1	sig F = 0.1110 F = 2.92490	
Y4	X1	sig F = 0.0483 F = 4.75110	- X1 is significant to Y4
Y5 (Supranol)	X1	sig F = 0.3119 F = 1.10704	
Y6 (Supranol)	X1	sig F = 0.1996 F = 1.82603	
Y5 (Kayacyl)	X1	sig F = 0.4866 F = 0.51274	
Y6 (Kayacyl)	X1	sig F = 0.4868 F = 0.51228	
Y7	X1	F is undefined	

TABLE 4.2b (continued)

Dependent variables	Independent variables	Result	Conclusion
Y1	X2	sig F = 0.7980 F = 0.06825	
Y2	X2	sig F = 0.0185 F = 7.24972	- X2 is significant to Y2
Y3	X2	sig F = 0.0711 F = 3.86281	
Y4	X2	sig F = 0.7037 F = 0.15123	
Y5 (Supranol)	X2	sig F = 0.3439 F = 0.96496	
Y6 (Supranol)	X2	sig F = 0.5939 F = 0.29881	
Y5 (Kayacyl)	X2	sig F = 0.9510 F = 0.00392	
Y6 (Kayacyl)	X2	sig F = 0.9463 F = 0.00471	
Y7	X2	sig F = 0.4544 F = 1.33333	

TABLE 4.2b (continued)

Dependent variables	Independent variables	Result	Conclusion
Y1	X1,X2	sig F = 0.0128 F = 6.40951	- X1 and X2 are significant to Y1
Y2	X1,X2	sig F = 0.0046 F = 8.71428	- X1 and X2 are highly significant to Y2
Y3	X1,X2	sig F = 0.0410 F = 4.21696	- X1 and X2 are significant to Y3
Y4	X1,X2	sig F = 0.1403 F = 2.32351	
Y5 (Supranol)	X1,X2	sig F = 0.3837 F = 1.03873	
Y6 (Supranol)	X1,X2	sig F = 0.3889 F = 1.02274	
Y5 (Kayacyl)	X1,X2	sig F = 0.7914 F = 0.23860	
Y6 (Kayacyl)	X1,X2	sig F = 0.7912 F = 0.23878	
Y7	X1,X2	F is undefined	

TABLE 4.2b (continued)

Dependent variables	Independent variables	Result	Conclusion
Y3	Y1	sig F = 0.5440 F = 0.38819	
Y4	Y1	sig F = 0.1830 F = 1.97821	
Y5 (Supranol)	Y1	sig F = 0.1526 F = 2.30877	
Y6 (Supranol)	Y1	sig F = 0.1471 F = 2.37777	
Y5 (Kayacyl)	Y1	sig F = 0.8048 F = 0.06360	
Y6 (Kayacyl)	Y1	sig F = 0.8045 F = 0.06382	
Y7	Y1	sig F = 0.7012 F = 0.25723	

TABLE 4.2b (continued)

Dependent variables	Independent variables	Result	Conclusion
Y3	Y2	sig F = 0.0315 F = 5.80728	- Y2 is significant to Y3
Y4	Y2	sig F = 0.0083 F = 9.67267	- Y2 is highly significant to Y4
Y5 (Supranol)	Y2	sig F = 0.1526 F = 0.32484	
Y6 (Supranol)	Y2	sig F = 0.4565 F = 0.58913	
Y5 (Kayacyl)	Y2	sig F = 0.9124 F = 0.01258	
Y6 (Kayacyl)	Y2	sig F = 0.9145 F = 1.29324	
Y7	Y2	sig F = 0.7012 F = 0.25723	

TABLE 4.2b (continued)

Dependent variables	Independent variables	Result	Conclusion
Y3	Y1,Y2	sig F = 0.0942 F = 5.80728	
Y4	Y1,Y2	sig F = 0.0350 F = 4.49041	- Y1 and Y2 are significant to Y4
Y5 (Supranol)	Y1,Y2	sig F = 0.3692 F = 1.08406	
Y6 (Supranol)	Y1,Y2	sig F = 0.3647 F = 1.09835	
Y5 (Kayacyl)	Y1,Y2	sig F = 0.9369 F = 0.06555	
Y6 (Kayacyl)	Y1,Y2	sig F = 0.9375 F = 0.06488	
Y7	Y1,Y2	F is undefined	

where: X1 = $\mathrm{Mn(acac)_3}$ X2 = N,N'-MBA

Y1 = percentage grafting Y2 = percentage of homopolymer

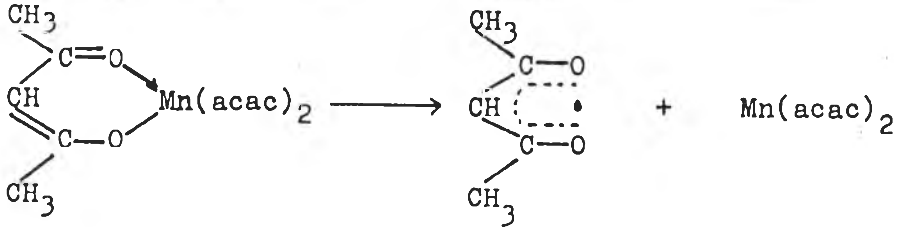
Y3 = tensile strength Y4 = percentage elongation

Y5 = quantity of dyestuff fixed on silk fibres

(S = Supranol, K = Kayacyl)

Y6 = percentage exhaustion Y7 = thermal decomposition temp.

The result from Table 4.2b shows that the percentage grafting data and the $Mn(acac)_3$ concentration values have a relationship with the significant F of 0.0027 [Appendix C]. Thus, the increase in initiator concentrations within the range of 0.5×10^{-3} to 2.5×10^{-3} mole-l^{-1} leads the increase in the yield of grafting. This finding supports the explanation pointed out by Arnett and Mendelsohn [14]. At the initial stages, the initiaton mechanism of $Mn(acac)_3$ is considered to occur through homolysis of the metal-oxygen bonds as shown in equation 4.1.


-------(4.1)

Otsu et al. [16] suggested further that the monomer molecule participates in the homolysis of $Mn(acac)_3$, i.e., in the initiating radical production step:

$$\mathrm{Mn(acac)_3} + \mathrm{M} \rightleftharpoons [\mathrm{M} > \mathrm{Mn(acac)_3}]$$
$$\downarrow$$
$$\mathrm{(acac)\text{-}M^{\cdot}} + \mathrm{Mn(acac)_2} \qquad \text{-------} \quad (4.2)$$

Accordingly, it can be concluded that the initiation of vinyl polymerization by using Mn(acac)$_3$ as initiator proceeds via a complex formation of the monomer, followed by homolysis of the metal-oxygen bond in the Mn(acac)$_3$ in order to result in an initiating radical.

A charge transfer complex is probably formed between the active groups on the silk backbone, the chelate and the monomer. Hence the concentrations of the chelate and the monomer increasingly gather in the vicinity of the fibres matrix; this thus assists in the homolysis of the metal-oxygen bond forming the acetylacetonate free radical ($R^{\cdot}$) as shown in equation 4.4.

Statistical methods were used to determine the interaction between the initiator and monomer in this particular experiment.

4.3 EFFECT OF N,N'-MBA CONCENTRATION ON GRAFT YIELD

The result of the percentage grafting formed with various concentrations of N, N'-MBA as monomer is tabulated in Table 4.1.

The effect of the concentration of N,N'-MBA within the range of 2.5×10^{-3} to 15.0×10^{-3} mole-l^{-1} on the grafting onto silk fibres is shown in Figure 4.3.

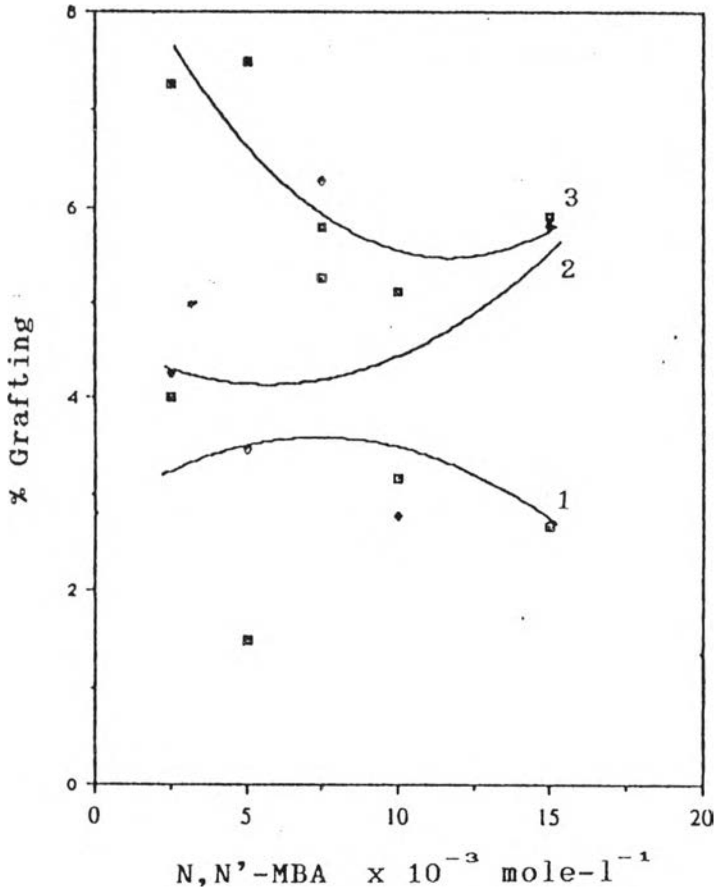


FIGURE 4.3 Effect of N,N'-MBA concentration on variation of % grafting

◻ 1 R = $Mn(acac)_3$ = 0.5 x 10^{-3} mole-l^{-1}

● 2 R = $Mn(acac)_3$ = 1.5 x 10^{-3} mole-l^{-1}

▣ 3 R = $Mn(acac)_3$ = 2.5 x 10^{-3} mole-l^{-1}

(Reaction condition : 50°C and 2 hrs)

According to Table 4.2a, the correlation coefficient (r) between the data of the percentage grafting and the concentration values of percentage grafting and concentrations of N,N'-MBA within the range of 2.5×10^{-3} to 15.0×10^{-3} mole-1^{-1} was -0.0723. This indicates that there is no linear relationship between the N,N'-MBA concentration values and the percentage grafting data. However, multiple regression method was used to analyze the relationship between these data.

The result from Table 4.2b shows that the percentage grafting data and the N,N'-MBA concentrations values have no relationship with the significant F of 0.7980 [Appendix C]. Thus, the use of N,N'-MBA may be less appropiate as grafting polymers for the silk under this condition; this may be possibly due to its bulky structure which can induce rigidity of the fibres.

4.4 EFFECT OF CONCENTRATION OF MANGANESE (III) ACETYLACETONATE ($Mn(acac)_3$) ON PERCENTAGE OF HOMOPOLYMER

The result of percentage of homopolymer with various concentrations of $Mn(acac)_3$ as initiator is shown in Table 4.1.

The effect of the concentration of $Mn(acac)_3$ on percentage of homopolymer is shown also in Figure 4.4.

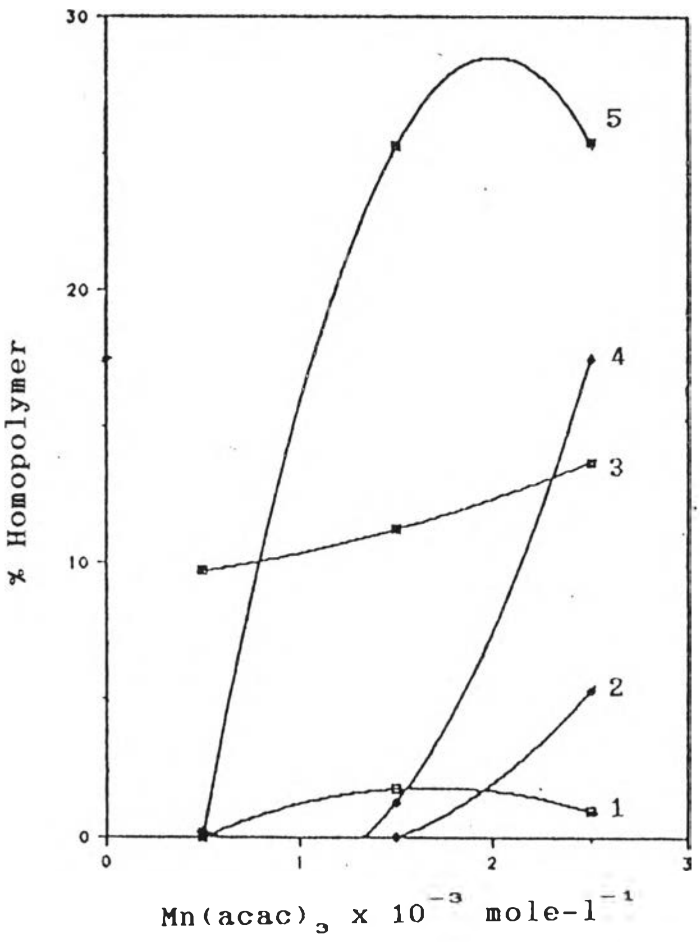


FIGURE 4.4 Effect of Mn(acac)$_3$ concentration on variation of % homopolymer

◘ 1 R = N,N'-MBA = 2.5 x 10^{-3} mole-l^{-1}

◆ 2 R = N,N'-MBA = 5.0 x 10^{-3} mole-l^{-1}

◘ 3 R = N,N'-MBA = 7.5 x 10^{-3} mole-l^{-1}

◆ 4 R = N,N'-MBA = 10.0 x 10^{-3} mole-l^{-1}

■ 5 R = N,N'-MBA = 15.0 x 10^{-3} mole-l^{-1}

(Reaction condition : 50°C and 2 hrs)

According to Table 4.2a, the correlation coefficient (r) between the percentage of homopolymer data and the concentration of Mn(acac)$_3$ within the range of 0.5 x 10^{-3} to 2.5 x 10^{-3} mole-l^{-1} was 0.4840. This indicates that there is no linear relationship between the Mn(acac)$_3$ concentration values and the percentage of homopolymer data. Like before, the multiple regression method was also used to analyze the relationship between these data.

The result from Table 4.2b, shows that the percentage of homopolymer data and the Mn(acac)$_3$ concentration values are independent with the significant F of 0.0676 [Appendix C].

As mentioned above, the increase in initiator concentrations clearly results in the increase in the percentage grafting. However, it should be noted that under the acid medium, the Mn(acac)$_3$ possibly dissociates to give the corresponding radicals which in turn initiate the homopolymer formation. The higher the initiator concentration is, the greater the homopolymer formation becomes. Homopolymer formation occurs rapidly and instantaneously, whereby the molecular weight of the homopolymer at higher initiator concentrations becomes smaller compared with those at appropriate concentrations.

4.5 EFFECT OF N,N'-MBA CONCENTRATION ON PERCENTAGE OF HOMOPOLYMER

The results of the percentage of homopolymer with various concentrations of N,N'-MBA as monomer are tabulated in Table 4.1.

The effect of the concentration of N,N'-MBA on the percentage of homopolymer is shown in Figure 4.5.

Statistical methods were used to analyze the parameter.

According to Table 4.2a, the correlation coefficient (r) between the percentage of homopolymer data and concentration values of N,N'-MBA within the range of 0.5×10^{-3} to 2.5×10^{-3} mole-l^{-1} was 0.5983. This indicates that there is no linear relationship between the N,N'-MBA concentration values and the percentage data of homopolymer. Again, multiple regression method was also used to analyze the potential relationship among these data.

From Table 4.2b, the result implies that the percentage of homopolymer significantly depends on the N,N'-MBA concentrations with the significant F of 0.0185 [Appendix C]. Thus, the increase in monomer concentrations

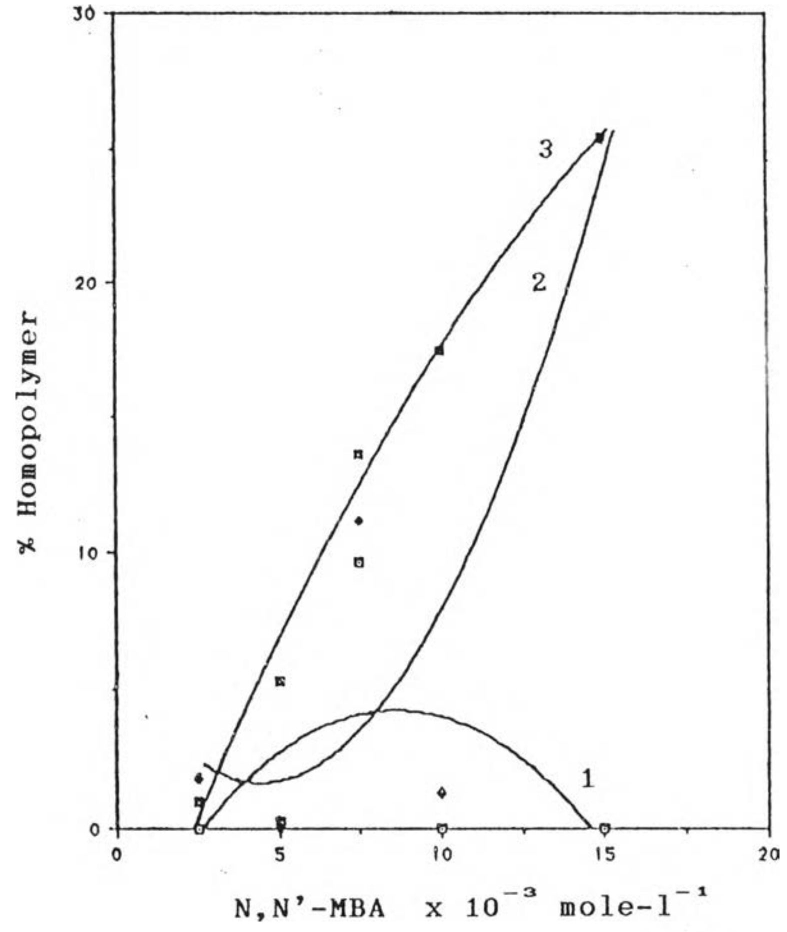


FIGURE 4.5 Effect of N,N'-MBA concentration on variation of % homopolymer

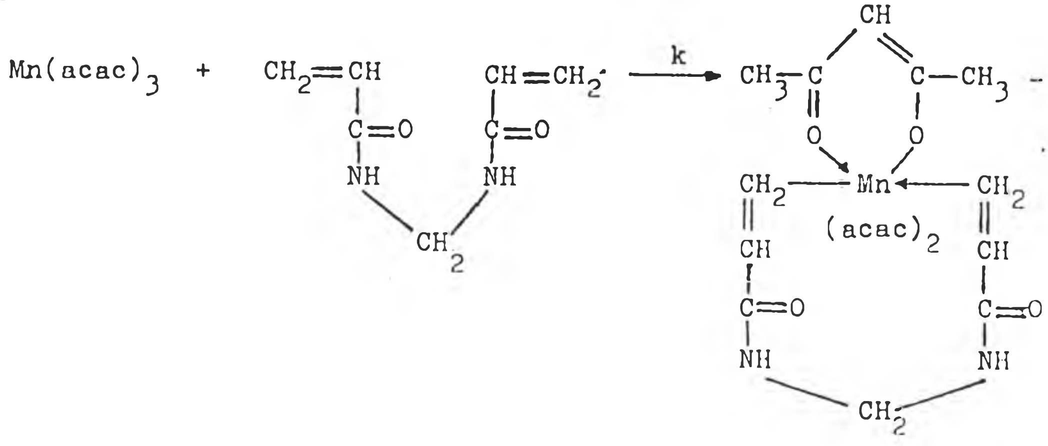
▫ 1 R = $Mn(acac)_3$ = 0.5 x 10^{-3} mole-l^{-1}

◆ 2 R = $Mn(acac)_3$ = 1.5 x 10^{-3} mole-l^{-1}

▪ 3 R = $Mn(acac)_3$ = 2.5 x 10^{-3} mole-l^{-1}

within the range of 2.5×10^{-3} to 15.0×10^{-3} mole-l^{-1}, in Figure 4.5, would result in the increase in the yield of homopolymer formation. The probable explanation for this finding might be due to the fact that at higher concentrations, the monomer molecules which do not associate with silk macroradicals can participate actively in the formation of linear homopolymer of N,N'-MBA. The investigation of the graft copolymerization mechanism of any vinyl monomer onto any trunk polymer, especially that naturally occurring, confirms that the homopolymer formation always accompanies the grafting reaction. The effect of monomer concentration thus inevitably plays a vital role affecting both polymers. The increase in the monomer concentration mostly favors the homopolymer formation because the monomer radicals are more likely to form one another rather than to graft on the trunk polymer. The following reaction steps are proposed to explain the results [4].

Radical formation: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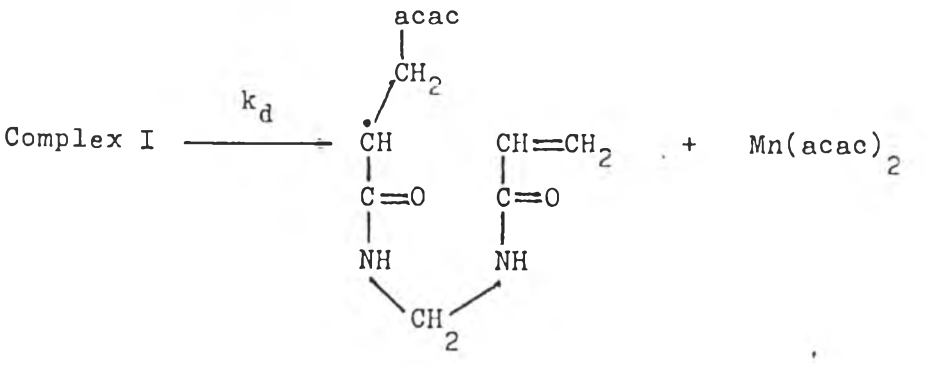
Complex I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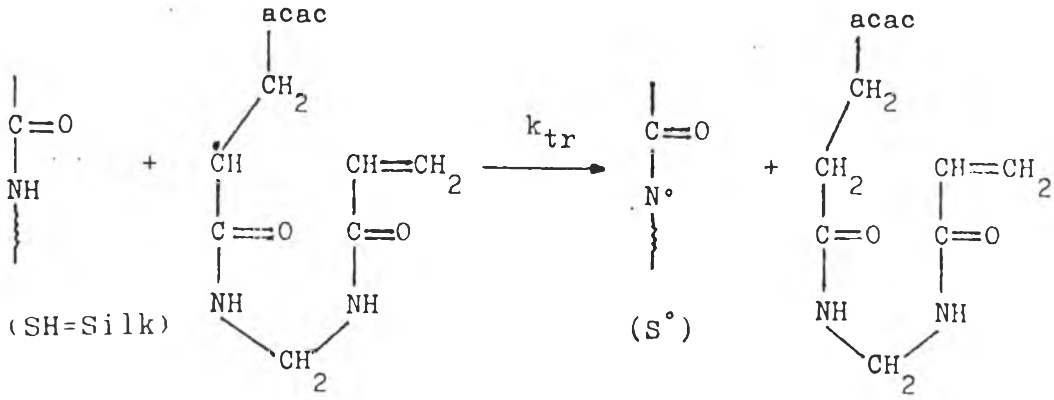
(R°)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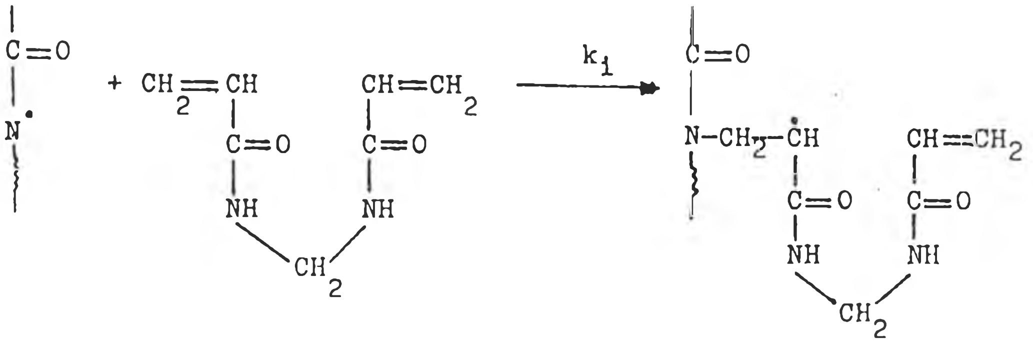
(SH=Silk)

(S°)

Initiation:



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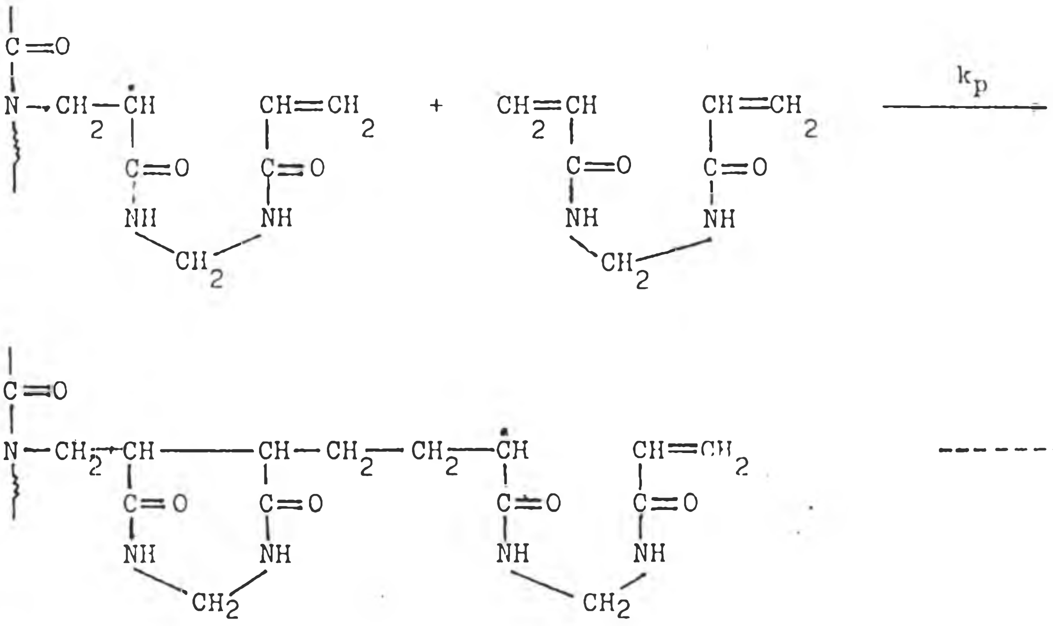
Propagation:



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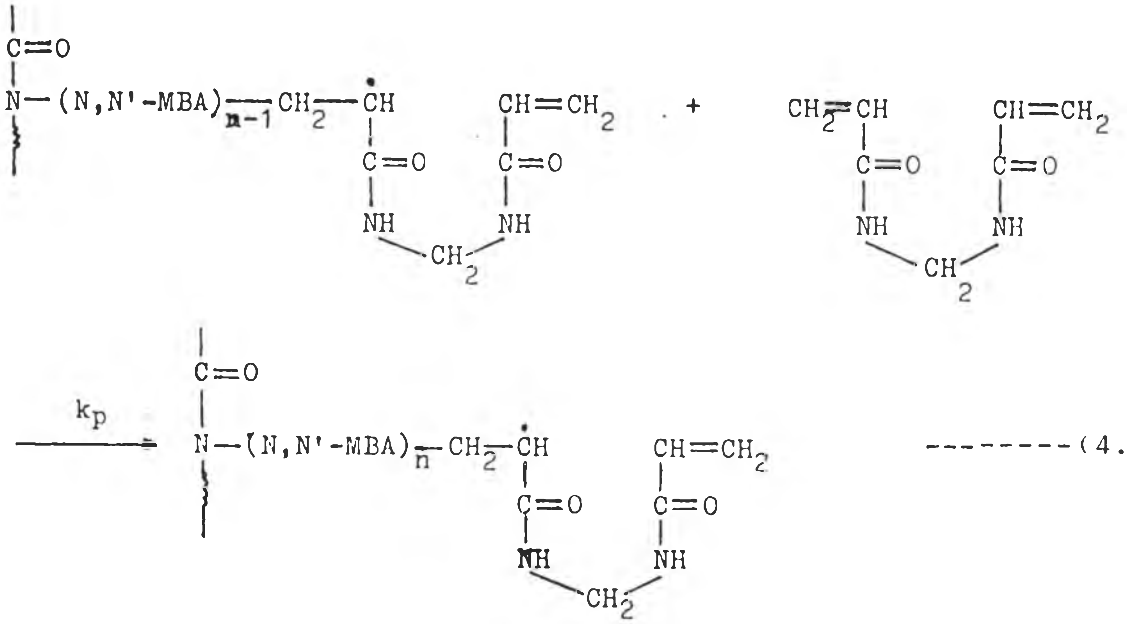

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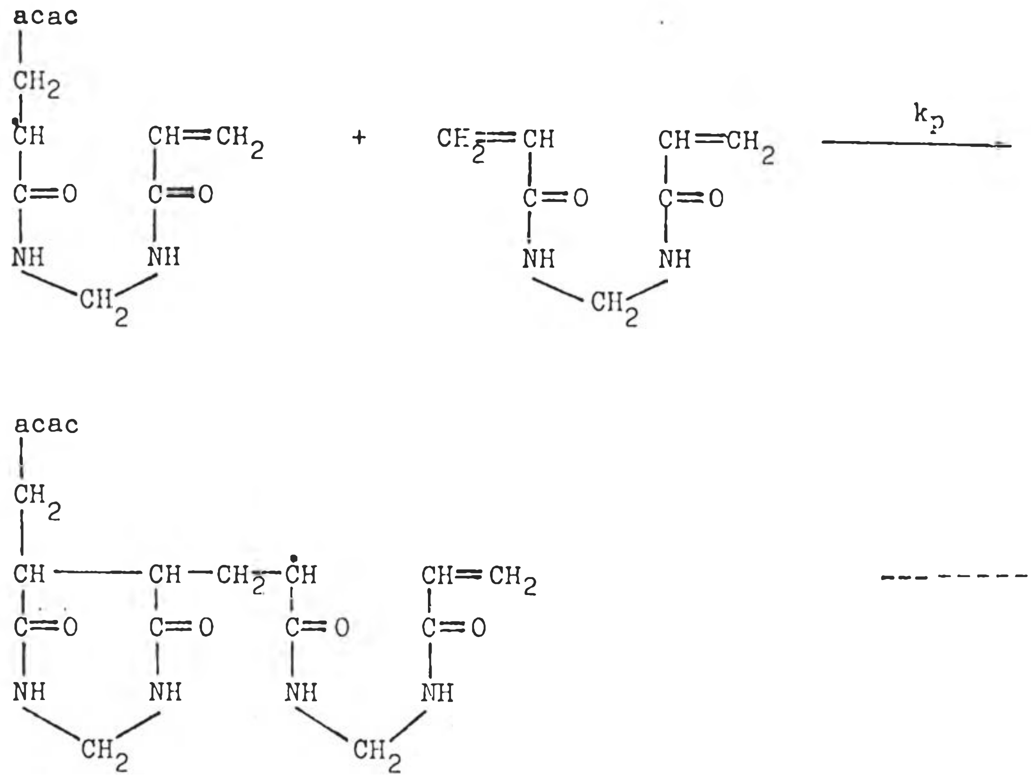
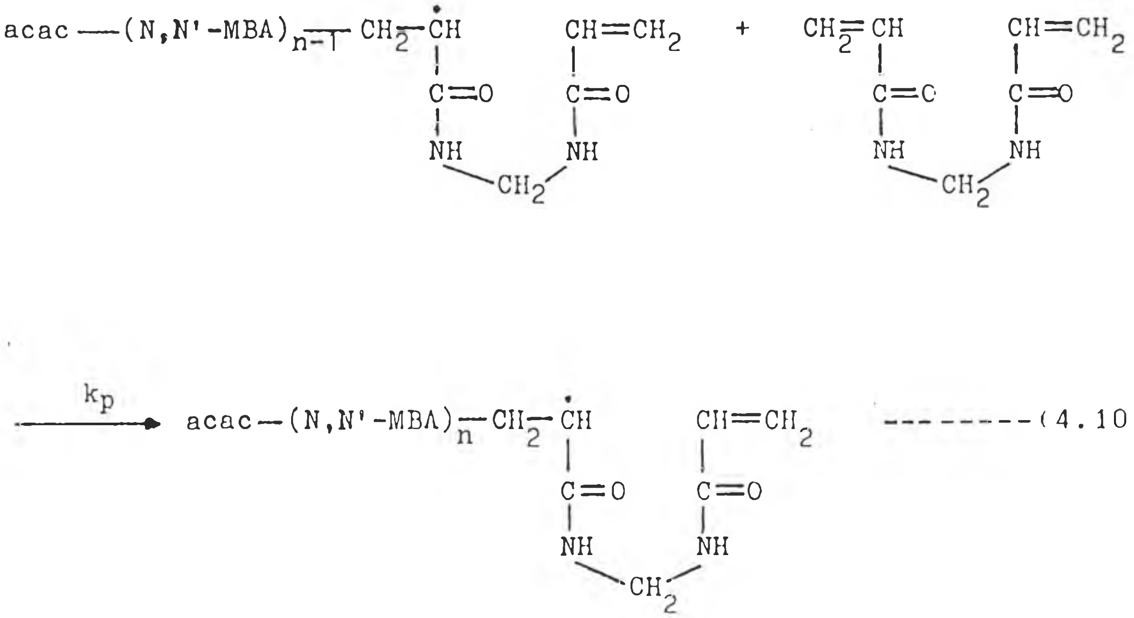


---------(4.9)



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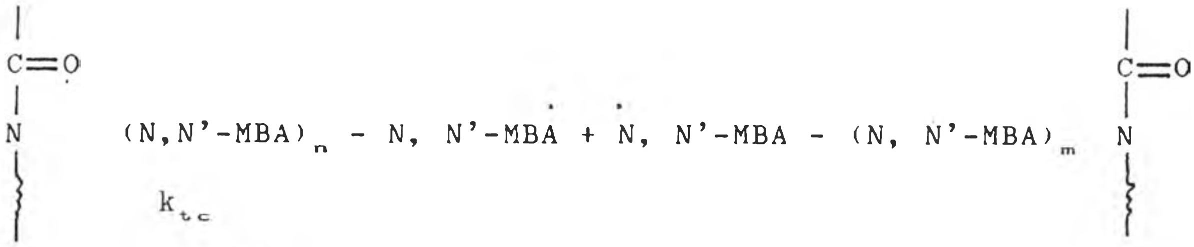
Termination:



$$\overset{\overset{|}{\text{C=O}}}{\underset{\wr}{N}}\quad (N,N'\text{-MBA})_n - N,\ N'\text{-MB}\dot{A} + \dot{N},\ N'\text{-MBA} - (N,\ N'\text{-MBA})_m\quad \overset{\overset{|}{\text{C=O}}}{\underset{\wr}{N}} \xrightarrow{k_{tc}} \text{grafted silk} \quad \ldots\ldots\ldots\ldots\ (4.11)$$

$$\text{acac} -(N,N'\text{-MBA})_n - N,N'\text{-MB}\dot{A} + \dot{N},N'\text{-MBA} - (N,N'\text{-MBA})_m\ \text{-acac} \xrightarrow{k_{tc}} \text{Homopolymer} \quad \ldots\ldots\ldots\ldots\ (4.12)$$

In addition, the rate of monomer radical diffusion seems to be high. This means that the very short kinetic chain lengths of the homopolymer are subsequently in existence. This results in the lower molecular weight of the homopolymer formed at higher monomer concentrations.

4.6 TENSILE STRENGTH AND PERCENTAGE ELONGATION

The tensile strength and elongation at break were measured and the results are presented in Table 4.3.

The effects of percentage grafting are shown in Figures 4.6a-4.6e.

TABLE 4.3 Effect of concentration of Mn(acac)$_3$ and N,N'-MBA on tensile strength and elongation of grafted silk fibres

Run	X1 [a] (mole-l^{-1}) x 10^{-3}	X2 [b] (mole-l^{-1}) x 10^{-3}	X3 [c] (mole-l^{-1}) x 10^{-3}	Y1 [d] (%)	Y3 [e] (gm)	Y4 [f] (%)
ungrafted	-	-	-	-	204	15
1A	0.5	2.5	5 x 0.5	4.0	207	13
1B	1.5	2.5	5 X 1.5	4.2	215	13
1C	2.5	2.5	5 X 2.5	7.2	209	12
2A	0.5	5.0	5 X 0.5	1.5	209	12
2B	1.5	5.0	5 X 1.5	3.5	215	13
2C	2.5	5.0	5 X 2.5	7.5	208	13
3A	0.5	7.5	5 X 0.5	5.3	220	13
3B	1.5	7.5	5 X 1.5	6.3	211	13
3C	2.5	7.5	5 X 2.5	5.8	165	10
4A	0.5	10.0	5 X 0.5	3.2	225	13
4B	1.5	10.0	5 X 1.5	2.8	183	13
4C	2.5	10.0	5 X 2.5	5.1	208	12
5A	0.5	15.0	5 X 0.5	2.7	200	15
5B	1.5	15.0	5 X 1.5	5.8	176	12
5C	2.5	15.0	5 X 2.5	5.9	184	11

[a] = Mn(acac)$_3$; [b] = N,N'-MBA; [c] = Glacial acetic acid

[d] = % grafting [e] = tensile strength; [f] = percentage elongation

([d] is 2 duplicates, [e] and [f] are 10 replicates within 10% CV)

under the set condition of [HClO$_4$] = 7.5 X 10^{-3} mole-l^{-1}, [NaLS] = 2.0 X 10^{-3} mole-l^{-1}, temp. = 50°C and time = 2 hrs

According to Table 4.2a, the correlation coefficient (r) between the percentage of homopolymer data and tensile strength values was -0.5557. This indicates that there is no relationship between the percentage of homopolymer and the tensile strength values, even in the opposite direction. As before, multiple regression method was also used to analyze the relationship among these data.

From Table 4.2b, the result implies that the tensile strength values significantly depend on the percentage of homopolymer, with the significant F of 0.0315. Thus, the increase in the percentage of homopolymer causes the tensile strength to decrease. The probable explanation for this finding might be due to the wastage of homopolymer formation. As the homopolymer formation increases, the grafting yield decreases accordingly. It should be noted that these two reactions usually compete with each other in the condition of normal graft copolymerization. The obtained 'r' value implies that the tensile strength decreases as the homopolymer formation reaction increases. This in turn affects the grafting efficiency. Deposited homopolymer, if any, should be removed from the silk surface since it does not provide any advantages to the silk fibres. Instead, it usually induces gloss reduction and problems in dyeing.

Note that the correlation coefficient (r) between the percentage grafting data and the tensile strength values does not indicate any significant linear relationship. However, the polynomial regression curves in Figures 4.6a-4.6d show that the concentrations of $Mn(acac)_3$ within the range of 0.5×10^{-3} - 2.5×10^{-3} mole-l^{-1} and N,N'-MBA concentrations of 2.5×10^{-3} - 10.0×10^{-3} mole-l^{-1} as the percentage grafting increases, the tensile strength slightly increases. However, in Figure 4.6e shows that with the concentrations of N,N'-MBA 15.0×10^{-3} mole-l^{-1}, as the percentage grafting increases, the tensile strength slightly decreases. Too high of an N,N'-MBA content on the silk fibres causes the fibres to become too rigid and consequently, tensile strength is reduced.

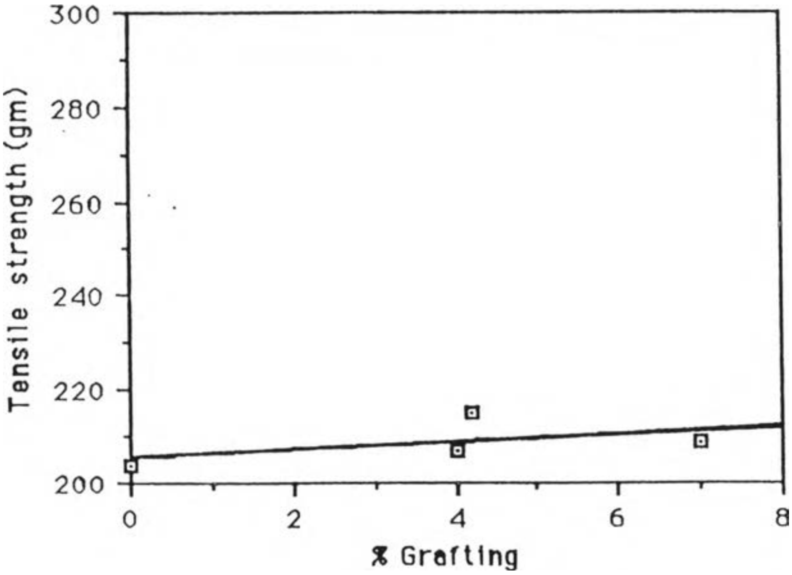


FIGURE 4.6a Tensile strength of N,N'-MBA-grafted silk fibres in relation to % grafting
$[Mn(acac)_3] = 0.5 \times 10^{-3} - 2.5 \times 10^{-3}$ mole-l^{-1}
$[N,N'\text{-MBA}] = 2.5 \times 10^{-3}$ mole-l^{-1}

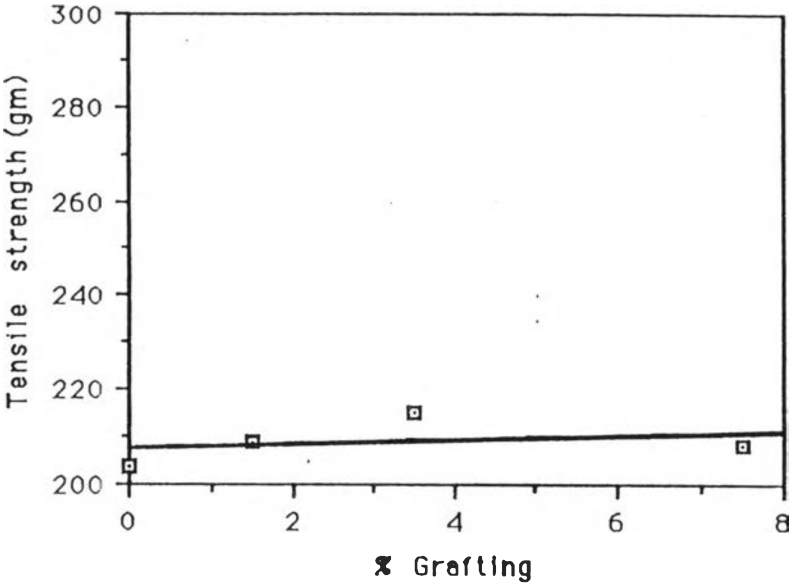


FIGURE 4.6b Tensile strength of N,N'-MBA-grafted silk fibres in relation to % grafting

$[Mn(acac)_3] = 0.5 \times 10^{-3} - 2.5 \times 10^{-3}$ mole-l^{-1}

$[N,N'\text{-}MBA] = 5.0 \times 10^{-3}$ mole-l^{-1}

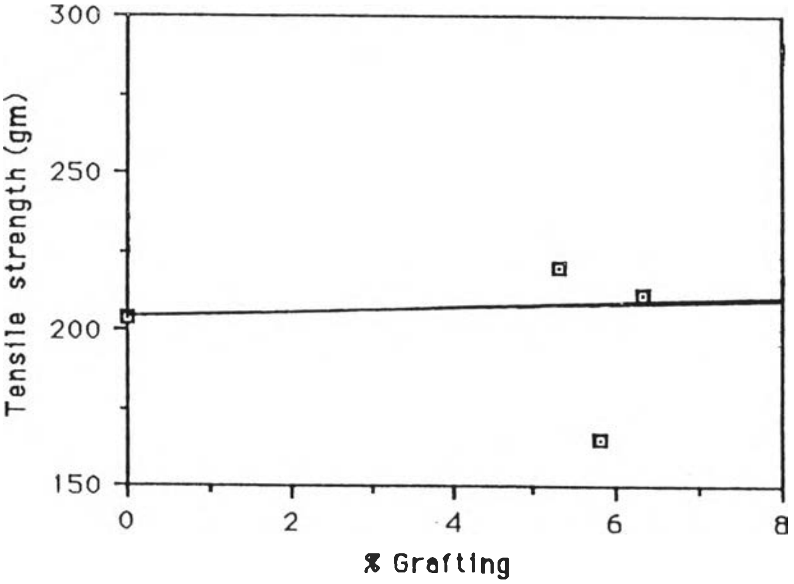


FIGURE 4.6c Tensile strength of N,N'-MBA-grafted silk fibres in relation to % grafting

$[Mn(acac)_3] = 0.5 \times 10^{-3} - 2.5 \times 10^{-3}$ mole-l^{-1}

$[N,N'\text{-}MBA] = 7.5 \times 10^{-3}$ mole-l^{-1}

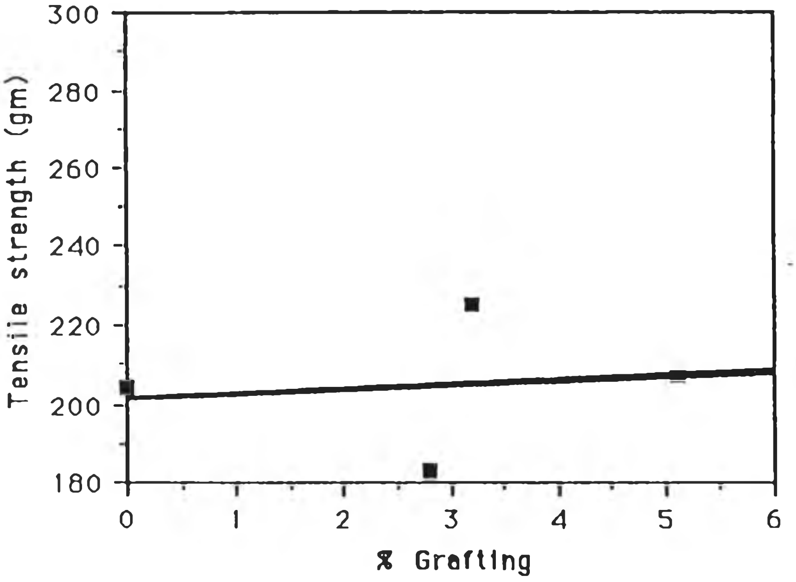


FIGURE 4.6d Tensile strength of N,N'-MBA-grafted silk fibres in relation to % grafting

$[Mn(acac)_3] = 0.5 \times 10^{-3} - 2.5 \times 10^{-3}$ mole-l^{-1}

$[N,N'-MBA] = 10.0 \times 10^{-3}$ mole-l^{-1}

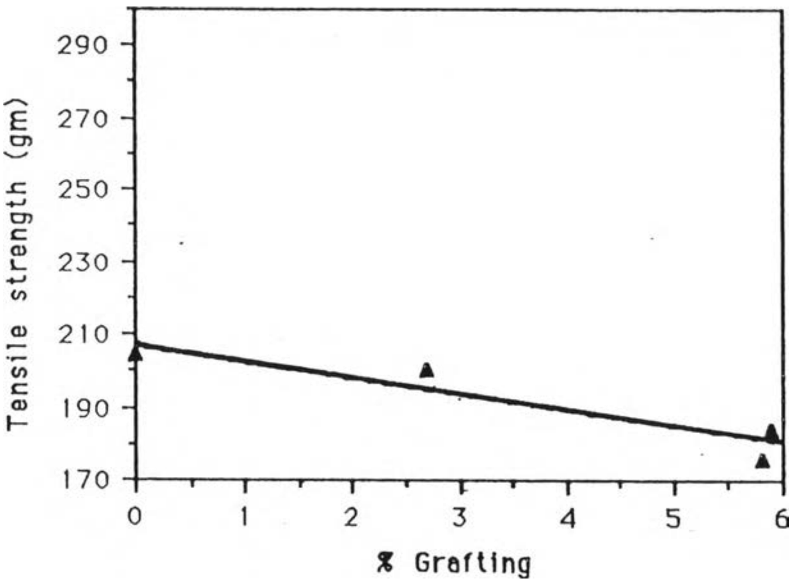


FIGURE 4.6e Tensile strength of N,N'-MBA-grafted silk fibres in relation to % grafting

$[Mn(acac)_3] = 0.5 \times 10^{-3} - 2.5 \times 10^{-3}$ mole-l^{-1}

$[N,N'-MBA] = 15.0 \times 10^{-3}$ mole-l^{-1}

It is interesting to note that there is no significant relationship between the initiator concentration and monomer concentration in this study as $r(x_1x_2$ or $x_2x_1 = 0)$.

4.7 THERMAL PROPERTY

The thermal behaviors of the recrystallized N,N'-MBA, the ungrafted silk fibres and the N,N'-MBA-grafted silk fibres were examined through the differential thermal analysis (DTA).

Figure 4.7 shows the DTA thermogram of the ungrafted silk fibres. Table 4.4 depicts general thermal properties of the ungrafted and N,N'-MBA grafted silk fibres. One general conclusion is that the higher the degree of graft incorporating the silk fibres is, the more thermal stability the grafted silk fibres have. The presence of N,N'-MBA on the silk fibres causes the increases in melting/ decomposition temperature. This results in the restriction of the whole chain movement.

The experiment on the graft copolymerize of N,N'-MBA onto the silk fibres supports the work of Tsukada and Shiozaki in that the polymerization treatment with MAN does not affect significantly the tensile properties, but does affect the thermal decomposition of the grafted polymers. The latter has the inclination to higher temperatures [26].

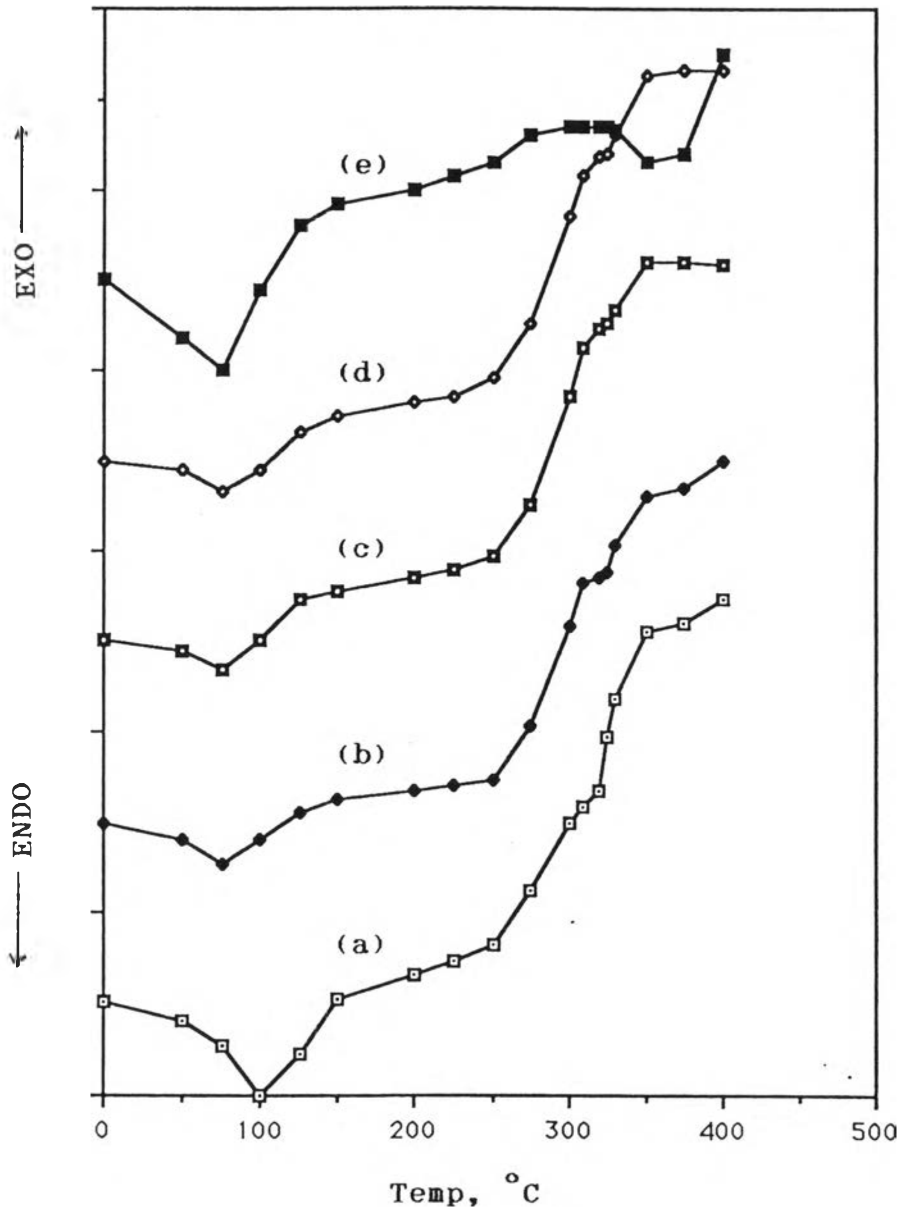


FIGURE 4.7 Thermal properties of ungrafted and N,N'-MBA - grafted silk fibres

-□-(a) = ungrafted silk -◆-(b) = 4 % grafting

-▣-(c) = 6 % grafting -◇-(d) = 7.5 % grafting

-■-(e) = Poly(N,N'-MBA)

TABLE 4.4 The thermal properties of ungrafted and N,N'-MBA-grafted silk fibres

Item	curve	%graft	%homopolymer	decomposition temperature °C[a]
Ungrafted	a	-	-	320
N,N'-MBA-grafted	b	3.99	0	324
N,N'-MBA-grafted	c	5.91	25.42	322
N,N'-MBA-grafted	d	7.50	5.27	326
Poly (N,N'-MBA)	e	-	-	366

[a] is the decomposition/melting temperature of silk fibroin fibres taken from the corresponding endothermic peaks.

4.8 DYEABILITY PROPERTY OF N,N'-MBA-GRAFTED SILK FIBRES

4.8.1 Dyeability Property of N,N'-MBA-Grafted Silk Fibres

The dyeing of silk fibres was carried out with acid dyestuff, Supranol Fast Orange GSN 140% and Kayacyl Sky Blue R. The method is described in Section 3.5.4.2. The quantity of the dyestuffs fixed on the ungrafted and grafted silk fibres and the percentage exhaustion are calculated below.

Supranol Fast Orange GSN 140%

Quantity of the dyestuff fixed on the silk fibres (D_F)

$$= 31.25\ A \qquad \text{..........}\ (4.13)$$

Kayacyl Sky Blue R

Quantity of the dyestuff fixed on the silk fibres (D_F)

$$= 36.76\ A \qquad \text{..........}\ (4.14)$$

where A = absorbance of the dye solution at its maximum absorption

The detailed derivation is shown in Appendix E.

Likewise, the percentage exhaustion of the solution is calculated below.

Supranol Fast Orange GSN 140%

percentage exhaustion =

$$\frac{\text{quantity of dyestuff fixed on silk fibres} \times 100}{16.25} \quad \ldots. \quad (4.15)$$

Kayacyl Sky Blue R

percentage exhaustion =

$$\frac{\text{quantity of dyestuff fixed on silk fibres} \times 100}{17.94} \quad \ldots. \quad (4.16)$$

The detailed derivation is shown in Appendix E.

Thus, the results of the quantity of the dyestuffs fixed on the ungrafted and grafted silk fibres and the percentage exhaustion are reported in Tables 4.5a and 4.5b.

TABLE 4.5a Dyeability property of N.N'-MBA -grafted silk fibres on Supranol Fast Orange GSN 140%

Run	X1[a] (mole-l^{-1}) x 10^{-3}	X2[b] (mole-l^{-1}) x 10^{-3}	X3[c] (mole-l^{-1}) x 10^{-3}	Y1[d] (%)	A[e]	Y5[f] =31.25A	Y6[g] $=\frac{Y5\ x100}{16.25}$
ungrafted	-	-	-	0.0	0.462	14.44	89
1A	0.5	2.5	5 X 0.5	4.0	0.404	12.63	78
1B	1.5	2.5	5 X 1.5	4.2	0.428	13.38	82
1C	2.5	2.5	5 X 2.5	7.2	0.421	13.16	81
2A	0.5	5.0	5 X 0.5	1.5	0.412	12.88	79
2B	1.5	5.0	5 X 1.5	3.5	0.375	11.72	72
2C	2.5	5.0	5 X 2.5	7.5	0.417	13.03	80
3A	0.5	7.5	5 X 0.5	5.3	0.426	13.31	82
3B	1.5	7.5	5 X 1.5	6.3	0.407	12.72	78
3C	2.5	7.5	5 X 2.5	5.8	0.418	13.06	80
4A	0.5	10.0	5 X 0.5	3.2	0.407	12.72	78
4B	1.5	10.0	5 X 1.5	2.8	0.407	12.72	78
4C	2.5	10.0	5 X 2.5	5.1	0.418	13.06	80
5A	0.5	15.0	5 X 0.5	2.7	0.394	12.31	76
5B	1.5	15.0	5 X 1.5	5.8	0.398	12.44	77
5C	2.5	15.0	5 X 2.5	5.9	0.414	12.94	80

[a] = Mn(acac)$_3$; [b] = N,N' -MBA; [c] = Glacial acetic acid

[d] = % grafting; [e] = absorbance

[f] = quantity of dyestuff fixed on silk fibres

[g] = percentage exhaustion

([d], [e], [f] and [g] are 2 duplicates within 10% CV)

under the set condition of [HClO$_4$] = 7.5 X 10^{-3} mole-l^{-1}, [NaLS] = 2.0 X 10^{-3} mole-l^{-1}, temp. = 50°C and time = 2 hrs

TABLE 4.5b Dyeability property of N.N'-MBA -grafted silk fibres on Kayacyl Sky Blue R

Run	X1 [a] (mole-l^{-1}) x 10^{-3}	X2 [b] (mole-l^{-1}) x 10^{-3}	X3 [c] (mole-l^{-1}) x 10^{-3}	Y1 [d]	A [e]	Y5 [f] =36.76A	Y6 [g] Y5 x 100 17.94
ungrafted	-	-	-	0.0	0.476	17.50	97
1A	0.5	2.5	5 X 0.5	4.0	0.397	14.59	81
1B	1.5	2.5	5 X 1.5	4.2	0.438	16.10	90
1C	2.5	2.5	5 X 2.5	7.2	0.444	16.32	91
2A	0.5	5.0	5 X 0.5	1.5	0.440	16.17	90
2B	1.5	5.0	5 X 1.5	3.5	0.455	16.73	93
2C	2.5	5.0	5 X 2.5	7.5	0.443	16.26	91
3A	0.5	7.5	5 X 0.5	5.3	0.425	15.62	87
3B	1.5	7.5	5 X 1.5	6.3	0.441	16.21	90
3C	2.5	7.5	5 X 2.5	5.8	0.423	15.55	87
4A	0.5	10.0	5 X 0.5	3.2	0.424	15.59	87
4B	1.5	10.0	5 X 1.5	2.8	0.434	15.95	89
4C	2.5	10.0	5 X 2.5	5.1	0.440	16.17	90
5A	0.5	15.0	5 X 0.5	2.7	0.438	16.10	90
5B	1.5	15.0	5 X 1.5	5.8	0.454	16.69	93
5C	2.5	15.0	5 X 2.5	5.9	0.410	15.07	84

[a] = Mn(acac)$_3$; [b] = N,N' -MBA; [c] = Glacial acetic acid

[d] = % grafting; [e] = absorbance

[f] = quantity of dyestuff fixed on silk fibres

[g] = percentage exhaustion

([d], [e], [f] and [g] are 2 duplicates within 10% CV)

under the set condition of [HClO$_4$] = 7.5 X 10^{-3} mole-l^{-1},

[NaLS] = 2.0 X 10^{-3} mole-l^{-1}, temp. = 50°C and time = 2 hrs

According to Table 4.2a, the correlation coefficient (r) between the percentage grafting values and quantities of the dyestuffs, "Supranol Fast Orange GSN 140%" and "Kayacyl Sky Blue R", fixed on silk fibres are 0.3883 and 0.0698, respectively. These values indicate that there are no linear relationships between the percentage grafting values and quantities of both dyestuffs fixed on silk fibres. Like before, multiple regression method was to analyze the relationships among these data.

The result from Table 4.2b shows that the quantities of dyestuffs fixed on the silk fibres insignificantly depend on the percentage values of graft. The obtained significant F values are 0.5784 and 0.9124 for Supranol and Kayacyl, respectively [Appendix C]. However, the only conclusion that can be drawn from the experiment is that the quantities of dyestuffs on the N,N'-MBA-grafted silk fibres can be reduced when compared to those on ungrafted silk fibres, as shown in Tables 4.5a and 4.5b.

It should be noted that the acid dyestuffs on the N,N'-MBA-grafted silk fibres surface have less opportunity for hydrogen bonding formation. This is due to the fact that their planar configurations are altered and that the bulkiness of N,N'-MBA hinders the accessibility of the acid dyestuffs to the silk surface. Consequently, Van der Waals force comes to function more effectively. This force is relatively weak and quite unstable, and thus gives the lesser dyeing property.

4.9 SURFACE CHARACTERISTICS

The surface characteristics of N,N'-MBA-grafted silk fibres were investigated by using a scanning electron microscopic technique. Figures 4.8a - 4.8d show the scanning electron micrographs of the surface of the ungrafted and N,N'-MBA-grafted silk fibres.

The electron micrographs reveal that the surface of the ungrafted silk fibres is even and smooth whereas the grafted silk fibres are uneven and rough. The latter is possibly due to unsteady deposit of the N,N'-MBA, especially when the graft yield is higher than 4 percent. The electron micrographs c) and d) show granular-like particles sticking uniformly on the surface. Besides the result of polymerization treatment, another speculation is that the separation of fibrils from the silk fibres could probably occur during grafting reaction and dyeing step.

FIGURE 4.8a Scanning electron micrograph of ungrafted silk fibres (x 750)

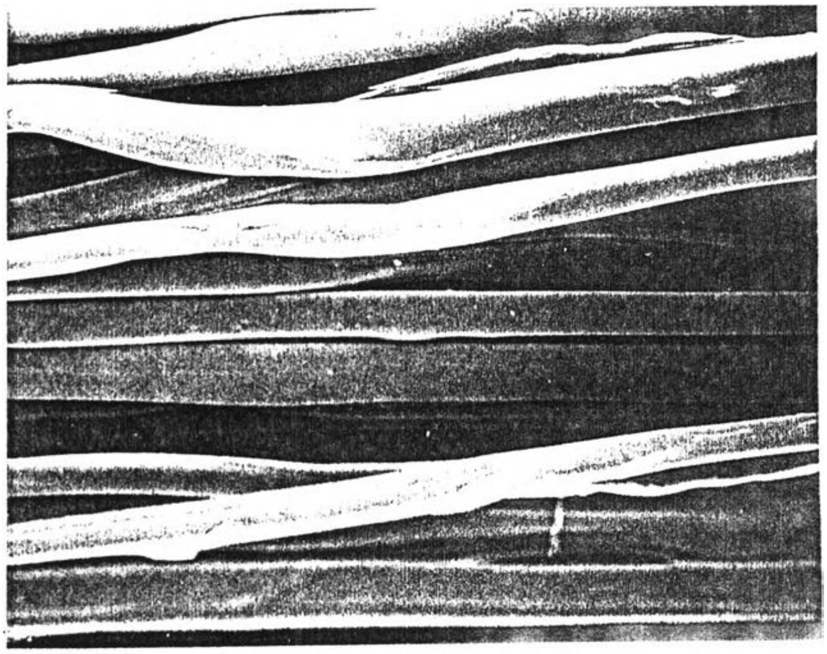


FIGURE 4.8b Scanning electron micrograph of N,N'-MBA - grafted silk fibres (4% grafting) (x 750)

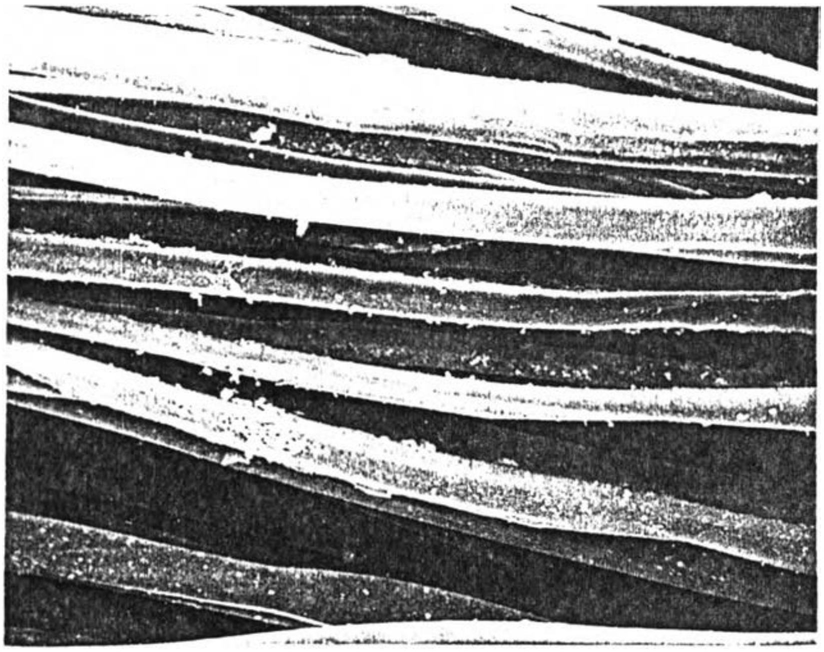


FIGURE 4.8c Scanning electron micrograph of N,N'-MBA - grafted silk fibres (6% grafting)(x 750)

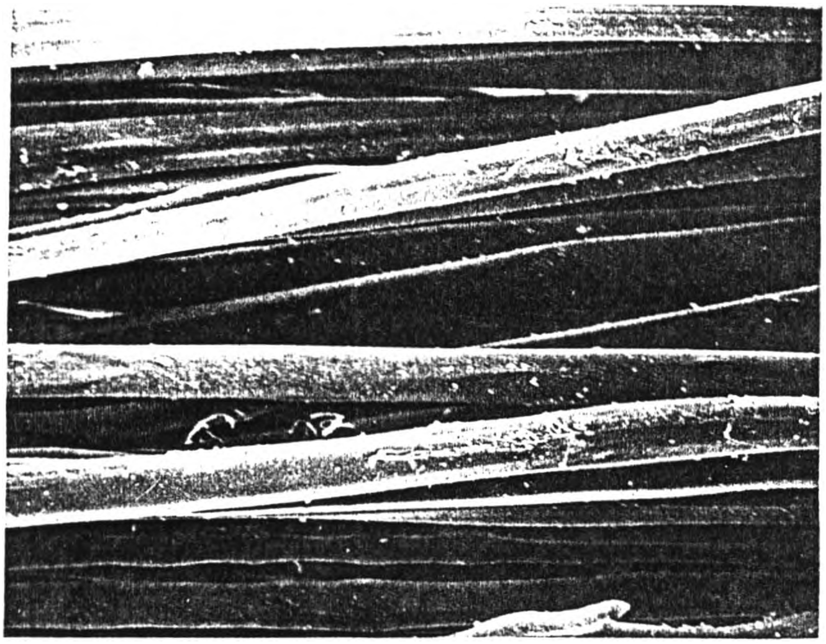


FIGURE 4.8d Scanning electron micrograph of N,N'-MBA - grafted silk fibres (7.5% grafting)(x 750)